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METHODS FOR BLEACHING OF CELLULOSIC MATERIALS

Technical Field

5 The present invention relates to a method and bleaching medium for bleaching cellulosic material. More particularly, the present invention relates to the use of an additive that improves the performance of bleaches, such as peroxide, oxygen and ozone, on cellulosic
10 materials.

Background of the Invention

15 Cellulosic materials such as cotton and wood pulp are subjected to bleaching to increase whiteness.

 Historically, chlorine bleaching agents have been fairly widely used for this purpose, however these are gradually being phased out of use because of the adverse environmental impact of the release of organohalogens
20 (AOX) during chlorine bleaching.

 The alternative agents for use in bleaching cellulosic materials are peroxide (such as hydrogen peroxide), oxygen and ozone. Of these, peroxide is the most commonly used. Peroxide bleaching of cellulosic
25 materials typically requires severe conditions including high temperatures, high alkali concentration, high chemical (bleaching agent) concentration and long exposure/treatment times. These operating conditions not only impose high production costs and environmental
30 damage, but they also lead to undesirable fibre and product performance.

 There is currently an interest and demand for more effective non-chlorine based bleaching methods that are able to provide an adequate bleaching action under
35 milder treatment conditions and thus minimise degradation of the desirable qualities of the cellulosic material.

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To date, a number of methods have been proposed for achieving this. Generally these methods involve the use of a bleaching assistant, activator or agent to enhance the bleaching effect of chlorine-free bleaches under milder treatment conditions. US patent nos. 4,392,975 and 5,034,096 describe methods for bleaching textiles and wood pulps using hydrogen peroxide assisted by cyanamide and derivatives thereof for improving the bleaching performance of hydrogen peroxide.

US patent nos. 6,248,209 and 6,342,124 describe methods of bleaching paper pulp using hydrogen peroxide or oxygen assisted by polyether compounds of a particular formula.

US patent no. 3,425,786 describes a method of bleaching textiles containing cotton using hydrogen peroxide assisted by N,N'-diacyl-methylene-diiformamide.

US patent nos. 5,145,558 and 5,013,404 and European patent no. EP 0639666 describe methods of bleaching paper pulp using hydrogen peroxide assisted by quaternary ammonium compounds.

US patent no. H479 describes a method of bleaching paper pulp using hydrogen peroxide assisted by alkenylsuccinic anhydride.

In addition to the above examples, there is presently available a low temperature bleaching process for bleaching cellulosic substrates using a hydrogen peroxide bleaching agent in combination with tetraacetythylenediamine (TAED). TAED has poor water solubility which can prevent it from being used in some commercial applications.

All the above methods suffer from various drawbacks, one of them being that they are not sufficiently efficient and effective for industrial bleaching practice.

Numerous bleach activators and peroxy acid bleaching precursors have also been developed to improve the stain removal capability of laundry detergents. The

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use of carboxylic acid ester peroxy acid precursors in laundry detergents has been described in Great Britain patent GB 836988, European patent EP0120591 and US patent no. 3,272,750. Other examples of peroxy acid precursors
5 are quaternary ammonium compounds and cationic nitriles, both of which have been described in the context of laundry detergents in European patents EP0284292, EP0331229, EP0303520 and EP0458396. However, the peroxy acid bleaching precursors used in laundry detergents for
10 improving stain removal are often not suitable for bleaching the full range of cellulosic materials such as paper pulps. Likewise, agents suitable for bleaching paper pulps are often not suitable for detergent use.

Accordingly, there is still a need for an
15 alternative method and bleaching medium that is efficient and effective in industrial bleaching operations.

Summary of the Invention

20 According to the present invention there is provided a method of bleaching a cellulosic material comprising contacting the cellulosic material with a bleaching agent selected from peroxide, oxygen, ozone or a mixture thereof, in the presence of a substituted
25 guanidine-based additive.

The substituted guanidine-based additive can be in the form of a salt. This may be useful if the non-salt form of the substituted guanidine-based additive used is not itself very water soluble. In general, substituted
30 guanidine-based compounds with good water solubility are particularly suitable for use in the present invention.

Although a large range of substituted guanidine-based additives are effective, the preferred classes are the alkyl guanidines, acyl guanidines and the alkyl acyl
35 guanidines. These substituted guanidine-based additives perform especially well in enhancing the performance of peroxide, oxygen and ozone bleaching agents in cellulose

bleaching processes.

It has also been found that the substituted guanidine-based additive can be used in conjunction with a peroxy acid precursor to achieve a further improved bleaching effect or a synergistic activation/acceleration effect. The peroxy acid precursor is preferable one selected from O-acyl peroxy acid precursors, N-acyl peroxy acid precursors and cationic peroxy acid precursors including cationic nitriles. The present applicant has found that contacting the cellulosic material with the bleaching agent (preferably a peroxide), the substituted guanidine-based additive and a peroxy acid precursor provides substantial enhancement in bleaching action with reduced chemical and energy consumption.

The present invention also provides a bleach activator composition for use in bleaching cellulosic material, the bleaching activator composition containing a substituted guanidine-based compound and one or more components selected from the group consisting of stabilisers, buffers, surfactants and other formulating agents

The bleach activator composition preferably also contains a peroxy acid precursor. This composition may be in the form of a solution, concentrate or solid. If in the form of a concentrate or solid, it can be diluted with water prior to use in the bleaching process.

The present invention also provides for the use of a substituted guanidine-based compound as an additive in bleaching processes, or as a bleaching activator.

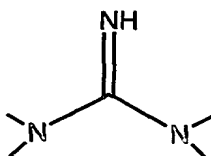
Detailed Description of the Invention

According to the method of the present invention, a substituted guanidine-based compound is used as an additive in the cellulose bleaching process.

The term "substituted guanidine-based additive" or "substituted guanidine-based compound" is used in its broadest sense to refer to any compound containing the

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group:



It is noted that the amine nitrogen atoms illustrated may
5 contain any substituent (as represented by the open-ended
bonds), but the imine nitrogen atom is unsubstituted. The
term encompasses aromatic and aliphatic guanidines and
derivatives thereof, as well as salts of the compounds
containing the group illustrated above. The term also
10 includes biguanide or biguanidine and derivatives thereof,
which compounds also contain the group illustrated.
However, the term does not encompass unsubstituted
guanidine, biguanide and biguanidine themselves.

Where compounds containing a single guanidine
15 unit only are intended, the term "monoguanidines" will be
used to distinguish from the broader class of guanidines
of which biguanide or biguanidine is a member.

Preferred substituted guanidine-based additives
are alkyl-, alkenyl-, alkynyl- and aryl- guanidines and
20 derivatives thereof, imino-, cyano-, sulfonyl-, halo-,
hydroxyl-, alkoxy- and acyl- guanidines and derivatives
thereof, and salts of the above.

As noted above, the substitute guanidine-based
additive may be a salt. Any organic or inorganic salt may
25 be used. Examples of suitable salts are hydrochloride,
sulphate, acetate and sulphonate.

A large number of substituted guanidine-based
compounds of a range of classes are commercially
available. These include phenylguanidine / biguanide;
30 halo-, alkyl- or alkoxy- phenylguanidine/ biguanide; 1-
benzylguanidine / biguanide and 1-benzoylguanidine.

Although a large range of substituted guanidine-

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based additives are effective, the more preferred classes are the alkyl guanidines, acyl guanidines and alkyl acyl guanidines.

5 These substituted guanidine-based additives perform especially well in enhancing the performance of peroxide, oxygen and/or ozone bleaching agents.

By way of explanation, "alkyl guanidine" refers to a derivative of guanidine in which at least one amine hydrogen atom is replaced with an alkyl group. Unless
10 otherwise indicated by the context, an alkyl guanidine, for example, can also be an acyl guanidine if another of the amine hydrogen atoms of guanidine is replaced with an acyl group. Such a compound may also be referred to as an alkyl acyl guanidine. It is also noted that the term
15 "alkyl guanidine", for instance, encompasses dialkyl, trialkyl and tetraalkyl guanidine.

The term "alkyl" used either alone or in compound words such as "aralkyl" refers to straight chain, branched chain or cyclic hydrocarbon groups having from 1 to 10
20 carbon atoms, preferably 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms. Illustrative of such alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

25 Preferably the alkyl group or groups are C1-C4 alkyl. More preferably, each alkyl group in the alkyl guanidines include 1 to 2 carbon atoms.

The term acyl guanidine is used to refer to guanidines containing at least one acyl group. Preferably
30 the acyl group or groups attach directly to one or both of the two amine nitrogen atoms.

The term "acyl" denotes (RC=O)-, in which R is H or any organic substituent, and encompasses carbamoyl, aliphatic acyl group, acyl group containing an aromatic
35 ring which is referred to as aromatic acyl, or an acyl group containing a heterocyclic ring which is referred to as heterocyclic acyl. The group R may contain from 0 to

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20 carbon atoms, preferably 1 to 14 carbon atoms.

Examples of acyl include carbamoyl, such as $-C(O)-NH_2$, $-C(O)NHCH_3$ and so forth; straight chain or branched alkanoyl, such as acetyl, propanoyl, butanoyl, 2-methylpropanoyl, octanoyl; alkoxy carbonyl, such as, ethoxycarbonyl, cycloalkyl carbonyl, such as cyclohexyl carbonyl; aroyl, such as, benzoyl, toluoyl or naphthoyl; and aralkanoyl, such as phenylalkanoyl, for example, phenylacetyl.

Where an acyl group is present, each acyl group is preferably aroyl (such as benzoyl), alkanoyl (such as acetyl) or a derivative thereof.

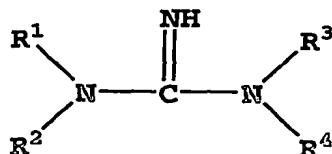
The term "imino" refers to a group containing a carbon to nitrogen double bond.

The alkyl, acyl and alkyl acyl guanidines may suitably be monoguanidines.

Where aryl groups are mentioned, the aryl group is preferably carbocyclic, such as phenyl, naphthyl and so forth. The most preferred substituted guanidine-based compounds contain no groups or substituents other than the alkyl and/or acyl groups.

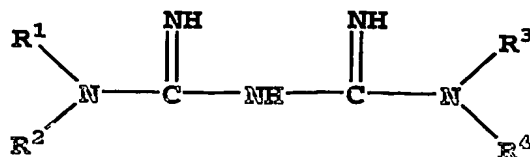
Either one type or a mixture of the substituted guanidine-based additives can be used.

In one embodiment of the invention, the substituted guanidine-based additive is of Formula I, Formula II or Formula III:

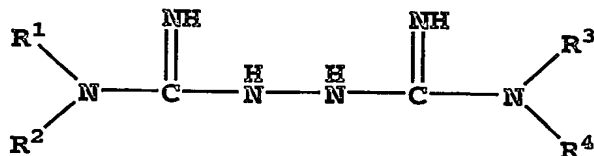


Formula I

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Formula II



Formula III

In each of formulae I, II and III,

5 R^1 is selected from the group consisting of alkyl or a derivative thereof, alkenyl or a derivative thereof, alkynyl or a derivative thereof, aryl or a derivative thereof, imino or a derivative thereof, cyano, halo, sulfonyl, hydroxyl, alkoxy or a derivative thereof and acyl or a derivative thereof, and

10 R^2 to R^4 are each independently selected from the group consisting of H, alkyl or a derivative thereof, alkenyl or a derivative thereof, alkynyl or a derivative thereof, aryl or a derivative thereof, imino or a derivative thereof, cyano, halo, sulfonyl, hydroxyl, 15 alkoxy or a derivative thereof, and acyl or a derivative thereof.

Compounds of Formulae II or III are commonly referred to as biguanides and biguanidines.

20 Any one or more of peroxide, oxygen and ozone can be used as the bleaching agent, however it is preferred for the bleaching agent to include peroxide. The term "peroxide" is used herein in the broadest sense to refer to all peroxide-containing or peroxide-releasing compounds 25 such as hydrogen peroxide sodium peroxide, peroxy acids,

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sodium perborate and sodium percarbonate. Hydrogen peroxide is the most commonly used peroxide.

It has also been found that the substituted
5 guanidine-based additive can be used in conjunction with a
peroxy acid precursor to achieve a further improved
bleaching effect or a synergistic activation/acceleration
effect. Peroxy acid precursors are reactive organic
compounds that in alkaline solutions containing a source
10 of hydrogen peroxide will generate the corresponding
peroxyacid. The peroxy acid may be a peroxy carboxylic
acid, a peroxy imidic acid, percarbonic acid, perboric
acid or similar. The conventional peroxy acid precursors
contain an O-acyl or N-acyl group, such as N,N,N'-
15 tetraacetythylenediamine (TAED) and nonanoylbenzene
sulphonate (NOBS). Other peroxy acid precursors are in
the form of a cationic peroxyacid precursor (see for
instance GB-A-1,382,594; US 4,751,015; EP-A-284,292 and
EP-A-331,229), including cationic nitriles (see EP-A-
20 303,520 and EP-A-458,396). The peroxy acid precursor is
preferably one selected from O-acyl peroxy acid
precursors, N-acyl peroxy acid precursors and cationic
peroxy acid precursors including nitrile.

Any other additives known in the art can also be
25 present during the bleaching process. Possible additives
include stabilisers, surfactants, buffers and alkali
sources. These are well known in the art of the invention.
Other additives referred to in the description of the
prior art set out above, including sulfonyl oximes,
30 organophosphoric azide, sulfonylimidazole, cyanamide and
disulfones may also be present. The additives used may
have more than one function.

It is contemplated that the substituted
guanidine-based additive or combination of the substituted
35 guanidine-based additive with a peroxy acid precursor
could be supplied in a pre-packaged form with other
components. Such components may help to maintain the

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guanidine-based additive or the additive combination in a solution, mixture or suspension form, or in a state resistant chemical change. Examples of these additional components include stabilisers, pH buffers and formulating agents.

The term "stabiliser" refers to an agent that controls the decomposition rate of the bleaching agent, and combines with metal impurities which may catalyse decomposition of peroxide and induce fiber damage. Stabilisers are well known in the art of the invention. Examples of bleaching stabilisers are the inorganic stabilisers, such as sodium silicate and polyphosphates, and the organic stabilisers such as aminocarboxylates (diethylenetriaminepentaacetic acid), hydroxycarboxylates (glucoheptonic acid) and organophosphonates [ethylenediaminetetra(methylenephosphonic acid) and diethylenetriaminepenta(methylenephosphonic acid)]. The organic stabilisers are more preferable to use in the pre-packaged activator formulations. These are sometimes referred to as sequestering or chelating agents.

The term "buffer" refers to an agent that minimises the change in the pH of a solution when an acid or base is added to the solution. Examples of suitable buffers are sodium acetate/acetic acid, citric acid/sodium citrate, potassium hydrogen phthalate/HCl and citric acid/disodium hydrogen phosphate.

The term "formulating agents" generally refers to additives such as surfactants, solvents, binders and encapsulating materials.

The term "surfactant" refers to a chemical substance having detergency, foaming, wetting, emulsifying and/or dispersing properties. Surfactants are well known in the art of the invention.

The invention can be implemented in most existing bleaching plants and processes that utilise hydrogen peroxide, oxygen or ozone with little or no alterations to the equipment of the plant. For instance, the present

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invention can be implemented with prior art methods known as "cold pad-batch", "pad-steam" and "exhaust" bleaching methods. These methods are particularly suited to bleach textiles and non-woven substrates containing cellulose.

5 The method of the present invention can be carried out over a broad range of operating conditions. The optimal operating conditions for the method will depend on, amongst other things, the precise nature of the substrate being bleached and the required properties of
10 the final product.

 Preferably, the substituted guanidine-based additive is used in an amount of 0.1 - 5.0% (more preferably 0.1 - 2.0%) by weight based on the amount of oven-dried pulp (in the case of bleaching cellulosic
15 material in pulp form), or in the amount of 0.1 - 3.0 g/L of bleaching solution (in the case of bleaching cellulosic material in textile form).

 In the situation where the bleaching agent is peroxide, preferably the peroxide is used in an amount of
20 0.2 to 5.0% (more preferably 0.5-2.0%) by weight based on the amount of oven-dried pulp, in the case of bleaching cellulosic material in pulp form. In the case of bleaching cellulosic material in textile form, preferably the peroxide is used in the amount of 1.0-10.0 g/L (more
25 preferably 2.0 - 6.0 g/L) of bleaching solution with the exhaust bleaching method, and 10.0-40.0 g/L (more preferably 15-25 g/L) with a cold pad-batch bleaching method.

 In the situation where a peroxy acid precursor is
30 also used, the ratio of a peroxy acid precursor to the substituted guanidine-based compound in the additive composition can, for example, range from 1:4 to 4:1. For many combinations of peroxy acid precursor and substituted guanidine-based compound tested, a 1:1 ratio was found to
35 be most suitable.

 The temperature at which the step of contacting the cellulosic material with the bleaching agent and

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substituted guanidine-based additive is conducted may be from ambient to over 100°C. Preferably the temperature is between 40°C and 80°C.

5 The pH is preferably between pH 9.0 and 12.0 when bleaching with peroxide and oxygen.

Generally speaking, as the temperature of the bleaching method increases, the pH of the bleaching solution or medium agent can be reduced. For example, at a temperature increase from 60°C to 80°C, the pH can be
10 reduced from 11.5 to 10.0.

The invention allows effective bleaching of substrates containing cellulose to be achieved using a bleaching agent containing hydrogen peroxide, oxygen or ozone over a broader range of pH and temperatures in
15 comparison to the prior art methods. Importantly, the present invention allows bleaching of substrates containing cellulose to be carried out at relatively mild operating conditions which reduces energy and bleaching agent consumption and preserves desirable qualities of the
20 substrate being bleached.

The method can be conducted on the broad range of cellulosic materials in a range of forms, including textile, non-woven and pulp forms. The cellulosic materials/fibres may include cotton; regenerated cellulose
25 fibres such as viscose, Tencel and cellulose acetate; bast fibres such as flax, hemp and jute; wood fibres and paper pulps; and other plant fibres such as sisal and straw. Pulp can be derived from wood fibres, nonwood fibres (as mentioned above) and recycled fibres. The term "cellulosic
30 material" also encompasses mixtures and/or blends of these cellulosic fibres with other materials.

The term "bleaching medium" is used broadly to refer to a bleaching liquid, concentrate or solution. The bleaching medium of the present invention contains at
35 least a bleaching agent selected from peroxide, oxygen, ozone or a mixture thereof, and a substituted guanidine-based additive. These are described above in full with

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respect to the method of the invention.

Illustrative Examples

5

The present invention will now be described with reference to the following non-limiting Examples.

Each Example consisted of a set of trials that
10 involved bleaching a cellulosic material with the control bleaching solution, and bleaching solutions of the present invention. The bleaching solutions of the present invention were made by adding a substituted guanidine-based additive of the present invention to the control
15 solution.

The substituted guanidine-based additives used in the following examples included:

	1,1-dimethylguanidine sulphate	(DMG)
	N,N,N'N'-tetramethylguanidine	(TMG)
20	1-Methylguanidine hydrochloride	(MG)
	1-Ethylguanidine sulphate	(EG)
	1,1-diethylguanidine sulphate	(DEG)
	1-benzoylguanidine hydrochloride	(BOG)
	1-Acetylguanidine	(ACG)
25	1,1-dimethylbiguanide hydrochloride	(DMBG)
	1-phenylbiguanide	(PBG)

In addition, the prior art additives N,N,N'N'-tetraacetylenediamine (TAED) and nonanoylbenzene
30 sulphonate (NOBS) were also investigated in comparison to the additives of the present invention.

Examples 1 to 6 involved the bleaching of various cellulose-containing textile substrates. The bleaching
35 trials were conducted on a Mathis Labomat at a liquor ratio of 20:1 (i.e. 20 millilitres of solution per gram of substrate).

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A control bleaching solution was prepared at room temperature, and an activator was added directly to the bleaching solution at room temperature. The bleaching bath was heated to a pre-selected temperature and held at the temperature for 60 to 90 minutes. The substrate was then rinsed with water, dried, and its whiteness was measured using a GretagMacbeth Color-Eye 7000A Spectrophotometer.

EXAMPLE 1. Bleaching of cotton with an alkylguanidine, alkylbiguanide or phenylbiguanide

The bleaching trials were conducted with unscoured greige cotton knitted fabric. The control bleaching solution consisted of the following:

Stabilisator 9188 (Böhme)	0.5 g/L
Surfactant	1.0-2.0 g/L
H ₂ O ₂ (50%)	5.0 g/L
NaOH	1.0 g/L

Sandozin MRN or Leonil JDZ and/or Hostapur SAS 60 (Clariant) was used as the surfactant.

Trial No.	Activator (1 g/L)	CIE Whiteness
1	Control (no activator)	61.6
2	TAED	63.2
3	MG	64.0
4	DMG	66.8
5	TMG	67.2
6	EG	63.5
7	DEG	63.5
8	DMBG	65.0
9	PBG	63.8

Trial No. 1 was carried out using the control

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solution without an activator, and Trial 2 was conducted with TAED. Trials No. 3 to Trial No. 9 were carried out using various substituted guanidine-based compounds. All trials were carried out at 60°C for 1 hour. The whiteness of the substrate achieved using any of the substituted guanidine-based additives was higher than the whiteness achieved by the control. Some of the guanidine-based activators were superior to TAED under the conditions examined.

EXAMPLE 2. Bleaching of cotton with DMG at various temperatures

The cotton fabric and control bleaching solution used in Example 2 were the same as that for Example 1.

The results shown in the Table indicate that DMG exhibits a significant activation effect over a temperature range from 40°C to 80°C.

Trial No.	Bleaching Temperature	CIE Whiteness	
		Control (no activator)	With DMG (1 g/L)
1	40°C	45.5	49.7
2	50°C	53.6	59.0
3	60°C	61.9	67.7
4	70°C	68.8	72.9
5	80°C	74.9	77.6

EXAMPLE 3. Bleaching of cotton fabric - A comparison of acyl- and alkyl- substituted guanidines with TAED and NOBS

Trials in Example 3 were conducted with an unscoured greige cotton fabric (knitted). The control bleaching solution consisted of:

Stabilisator 9188 0.5 g/L

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Surfactants 2.0 g/L
H₂O₂ (50%) 6.0 g/L
NaOH 1.2 g/L

5 The bleaching was carried out at 60°C for 1 hour.

Trial No.	Activator (0.8g/L)	CIE Whiteness
1	Control (no activator)	62.8
2	ACG	68.7
3	BOG	68.5
4	DMG	66.5
5	NOBS	67.1
6	TAED	66.0

10 The results in Example 3 show that 1-benzoylguanidine (BOG) and 1-acetylguanidine (ACG) are superior to TAED and NOBS in cotton bleaching under the conditions examined.

EXAMPLE 4. Bleaching of cotton fabric with a combination of TAED and DMG

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The bleaching trials were conducted with unscoured greige cotton knitted fabric. The bleaching solution consisted of the following:

20 Stabilisator 9188 (Böhme) 0.5 g/L
Surfactants 1.0-2.0 g/L
H₂O₂ (50%) 5.0 g/L
NaOH 2.0 g/L

The trials were carried out at 60°C for 1 hour.

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Trial No.	Activators Used	CIE Whiteness
1	Control (no activator)	65.0
2	2.0 g/L DMG	70.6

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3	2.0 g/L TAED	69.3
4	0.5 g/L TAED+0.5 g/L DMG	71.0
5	1.0 g/L TAED+1.0 g/L DMG	73.5

In addition to the superior bleaching performance achieved in Trial 2, the results of Example 4 show that the whiteness achieved using a bleaching solution containing mixtures of both DMG and TAED is higher than the whiteness achieved when only DMG or TAED is added to the bleaching solution.

EXAMPLE 5. Bleaching of a Cotton/Wool Blend

Trials in Example 5 were conducted with a woven cotton/wool (70%/30%) blend. The control solution consisted of the following:

Stabicol BAC (Ciba) 3.0 g/L
 Surfactants 1.5 g/L
 H₂O₂ (50%) 12.0 g/L

The trials were conducted out at 60°C for 80 minutes.

Trial No.	Activator (g/L)	CIE whiteness
1	Control	56.7
2	0.6 ACG	59.3
3	0.7 ACG	60.9
4	0.6 NOBS	58.1
5	0.6 TAED	57.4

It can be seen that under these conditions, ACG is a superior bleach activator for the peroxide bleaching of the cotton/wool blend.

EXAMPLE 6. Bleaching of Viscose Blends

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Trials in Example 6 were conducted with a viscose/polyester (76%/24%) blend. The control solution and bleaching conditions used were the same as in Example 5.

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Trial No.	Activator (0.6 g/L)	CIE whiteness
1	Control	67.5
2	ACG	69.9
3	DMG	70.5

The trials clearly demonstrate that DMG and ACG are effective activators in the bleaching of viscose blends. Similar results were obtained with a viscose/Lycra® (94%/6%) blend.

10

Examples 7 and 8 involved the bleaching of kraft pulps. The pulp samples were first de-watered in a mechanical press to about 30% consistency and crumbed. Samples of 50g each (o.d. basis) were then placed in a plastic bag and make up liquor and chemicals added to give a pulp consistency of 20 to 22%. The treated pulp was held in a waterbath or an oven at a set temperature for a certain number of hours.

15

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After bleaching, the bleached samples were washed and neutralised with dilute sulfuric acid.

The ISO brightness and CIE whiteness of bleached pulp samples were measured on a GretagMacbeth Color-Eye 7000A Spectrophotometer. The Kappa numbers of the pulps were determined according to Australian Standard method AS 1301.201m-86.

25

30 **EXAMPLE 7. Bleaching of a unbleached kraft pulp**

In Example 7, the trials were carried out using

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unbleached native forest eucalypt Kraft pulp from a commercial mill (with Kappa number 9.2).

- 5 A control bleaching solution consisted of the following:

Chemicals	% (on weight of o.d. pulp)
Sodium Silicate	1.5
H ₂ O ₂	1.0
NaOH	0.2

Trial No.	Activator (0.7% on o.d.pulp)	CIE Whiteness	ISO Brightness
1	Control	15.7	62.8
2	DMG	25.6	66.8

- 10 The trials were carried out at 55°C for 28 hours. The results demonstrate that the bleaching solution of the present invention also provides superior bleaching of the unbleached kraft pulp.

15 *EXAMPLE 8. Bleaching of O(EOP) pre-bleached kraft pulp*

- The kraft pulp sample used in Example 8 was pre-bleached with O(EOP) sequence, i.e. the commercial unbleached kraft pulp was oxygen-delignified, this stage was followed by a wash, then an oxygen-boosted alkaline extraction with addition of hydrogen peroxide. In standard notation this sequence is abbreviated as O(EOP), where O = oxygen, E = alkali extraction, and P = hydrogen peroxide. Bracketing the letters (EOP) together indicates that the three chemicals were added concurrently, i.e. without a wash stage between the chemical treatments. After this pre-bleaching sequence, the Kappa number was 4.1, and

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brightness was 64.5%.

The trials of Example 8 were carried out at the same conditions as that used in Example 7.

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Trial No.	Activator (1% on o.d.pulp)	CIE Whiteness	ISO Brightness
1	Control	59.7	81.4
2	DMG	66.5	85.2

The results show the substituted guanidine-based additive DMG provides a significant increase in brightness and whiteness of the O(EOP) kraft pulp.

10

While the present application has been illustrated by bleaching cotton, cotton blend, viscose blend and wood pulps, it is to be understood that all cellulosic materials may be bleached in an identical or similar fashion. Accordingly, the bleaching of all such materials using a substituted guanidine-based additive or combinations of this additive with other additives and/or activators known in the art is expressly within the scope of the present invention.

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It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

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